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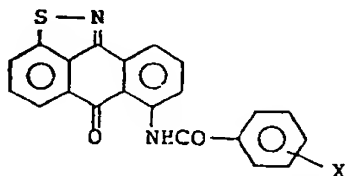
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64 Water-insoluble disperse dye composition.

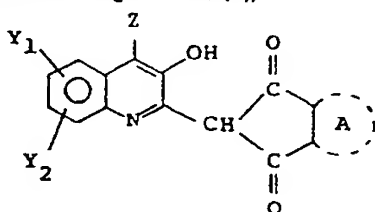
57 A water-insoluble disperse dye composition comprising a combination of a dye represented by the following formula (I).



(I)

wherein Z, Y₁ and Y₂ are independently hydrogen or halogen, and the ring A is a benzene or naphthalene ring unsubstituted or substituted with a carboxylic acid ester group, in an amount of 5 to 80% by weight, which is useful for dyeing polyester fiber materials to obtain dyed products having both extremely high light fastness and excellent thermal resistance.

wherein X is hydrogen, halogen, lower alkyl or lower alkoxy, in an amount of 95 to 20% by weight, and a dye represented by the following formula (II).



(II)

WATER-INSOLUBLE DISPERSE DYE COMPOSITION 0208211

1 The present invention relates to a water-insoluble disperse dye composition.

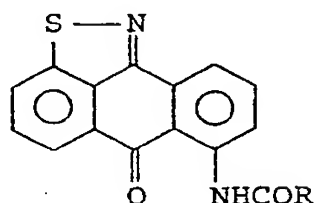
 More specifically, the present invention relates to a water-insoluble disperse dye composition useful for
5 dyeing fiber materials to obtain dyed products having extremely high light fastness.

 Recently, polyester fiber materials have been used increasingly as materials for car interior because of their excellent heat and light resisting properties.
10 With the increasing use, disperse dyes to be used for dyeing the polyester fiber materials have been required to have much excellent light fastness, particularly at a high temperature. In general, the fastness test to light is carried out according to JIS L-0842 in a manner
15 such that a dyed product is exposed to carbon arc lamp for 10 to 80 hours at a temperature of $63 \pm 3^{\circ}\text{C}$. While, in order to be used for the car interior, the dyed products are required to be resistant against exposure of carbon arc lamp for 400 to 600 hours at a temperature
20 as high as $83 \pm 3^{\circ}\text{C}$. Moreover, when used for car seats, the dyed polyester materials are put on urethane foam of a regeneration property, and therefore it is not seldom to allow the materials to stand at a temperature higher than $83 \pm 3^{\circ}\text{C}$. For these reasons, the disperse
25 dyes have been required to be resistant against much

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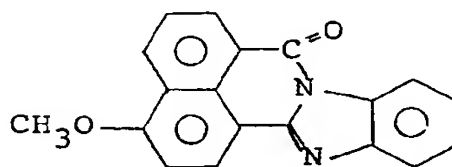
1 severe conditions.

As yellow dyes having excellent light fastness
usable for the utilities described above, the following
two compounds are known. One of them is represented
5 by the following formula (a),



(a)

wherein R is a lower alkyl group, and the other is
represented by the following formula (b),



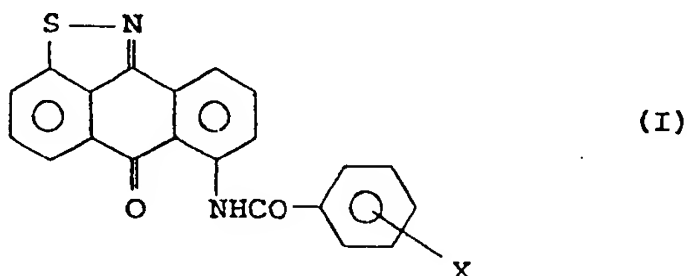
(b)

Generally speaking, in order to obtain a desired
color shade, two or more dyes of colors different from
10 each other are blended. When each of yellow dyes
described above is used for dyeing polyester fiber
materials in combination with another dye such as a red
dye, a blue dye or a mixture thereof, a color shade
obtained greatly changes after a processing such as heat
15 set treatment. This is because of their extremely poor

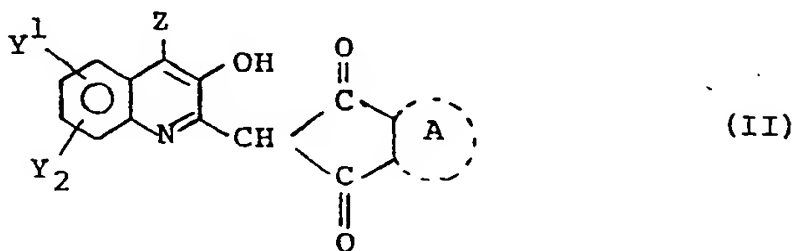
- 1 thermal resistance, by which many problems have often
 been caused on a practical use. Accordingly, a yellow
 disperse dye having both extremely high light fastness
 and excellent thermal resistance has been desired -
 5 particularly in the field of car interior.

The present inventors have undertaken extensive
 studies to find such yellow dye, and as a result found
 that a combination of specific yellow dyes can accomplish
 the object.

- 10 The present invention provides a water-insoluble
 disperse dye composition comprising a combination of a
 dye represented by the following formula (I),



- wherein X is hydrogen, halogen, C_1-C_4 alkyl or C_1-C_4
 alkoxy, in an amount of 95 to 20% by weight, and a dye
 15 represented by the following formula (II),

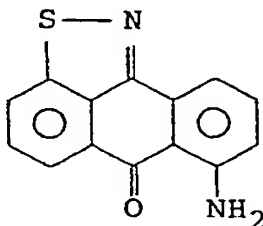


1 wherein Z, Y₁ and Y₂ are independently hydrogen or
halogen, and the ring A is a benzene or naphthalene ring
unsubstituted or substituted with a carboxylic acid
ester group, in an amount of 5 to 80% by weight.

5 The dye of the formula (I) is favorable in
light fastness and thermal resistance, but inferior in
exhaustion and build-up properties, by which problems
have been caused on a practical use, and the dye of the
formula (II) is insufficient in light fastness at a high
10 temperature, so that it is hardly used for dyeing
polyester fibers to obtain dyed products of extremely
high light fastness enough to be applied for car
interior.

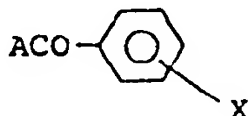
Notwithstanding such defects of the dyes (I)
15 and (II), a combination of them can exhibit extremely
high light fastness and excellent thermal resistance as
well as excellent exhaustion and build-up properties.

The dye of the formula (I) can be produced,
for example, by reacting a compound of the following
20 formula,



with a compound of the following formula,

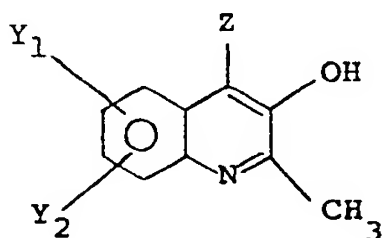
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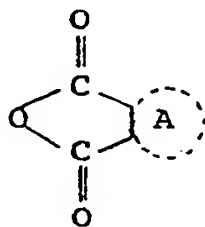
- 1 wherein X is as defined above, and A is a halogen, at a temperature of 50° to 150°C in an inert solvent.

The dye of the formula (II) can be produced, for example, by reacting a compound of the following

- 5 formula,



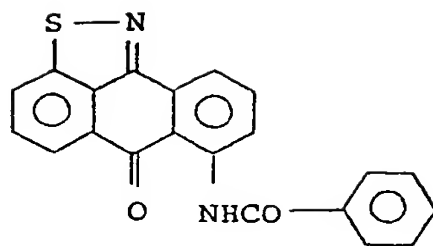
wherein Y₁ and Y₂ are as defined above, with a compound of the following formula,



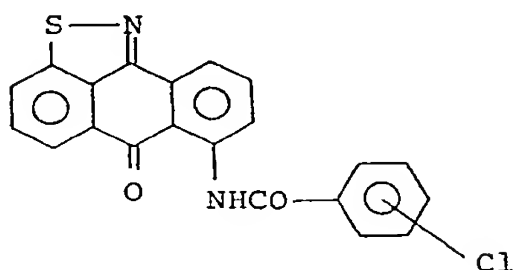
- wherein A is as defined above, at a temperature of 150° to 250°C in an inert solvent, if desired, followed by
10 halogenation.

Of these compounds, preferably used are those of the following formula,

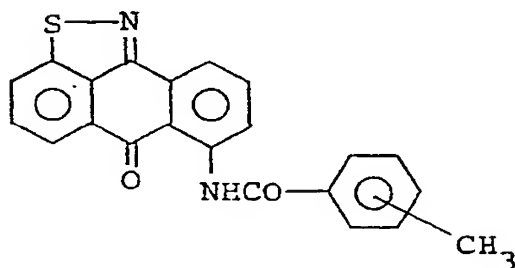
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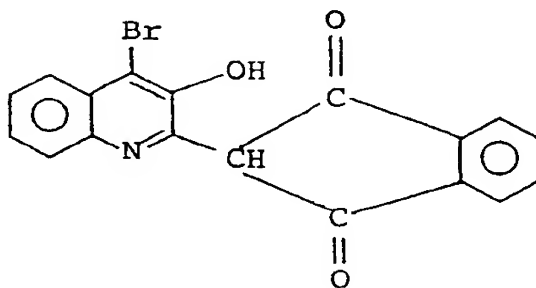
1 of the following formula,



and of the following formula,

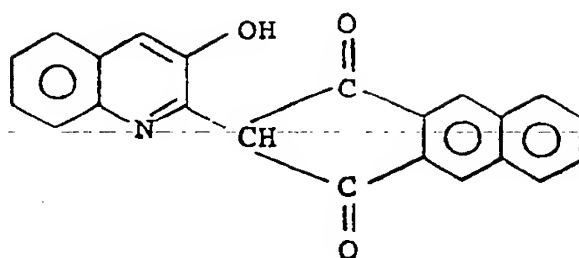


which are included in the formula (I), and used each alone or in a mixture thereof, and those of the following formula,

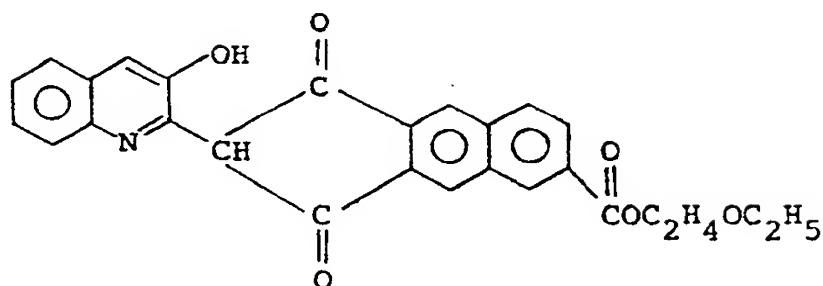


of the following formula,

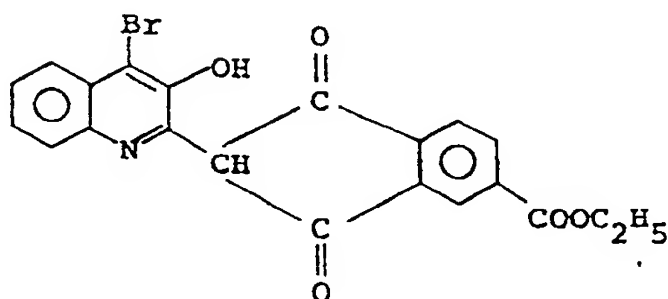
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of the following formula,

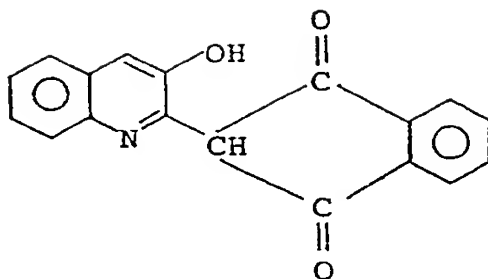


of the following formula,



and of the following formula,

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1 which are included in the formula (II), and used each alone or a mixture thereof.

The dye composition of the present invention can be prepared by mixing or blending the dye of the
5 formula (II) with the dye of the formula (I) at any time before a step for making a final product.

A weight ratio in the dye composition of the present invention is 95 to 20, preferably 90 to 50, of the dye (I), to 5 to 80, preferably 10 to 50 of the
10 dye (II).

The present dye composition may comprise usual additives such as ultraviolet ray absorbents. Examples of the ultraviolet ray absorbents are as follows:

15 2-(2'-Hydroxyphenyl)-5-chloro-benzotriazole

2-(2'-Hydroxy-4'-methylphenyl)-5-chloro-benzotriazole

2-(2'-Hydroxy-4'-ethylphenyl)-5-chloro-benzotriazole

20 2-(2'-Hydroxy-3'-t-butyl-5'-methylphenyl)-5-chloro-benzotriazole

- 1 2-(2'-Hydroxy-3',5'-di-t-butylphenyl)-5-
chloro-benzotriazole
- 2-(2',4'-Dihydroxyphenyl)-5-chloro-benzotriazole
- 2-(2'-Hydroxy-4'-propylphenyl)-5-chloro-
- 5 benzotriazole
- 2-(2'-Hydroxy-4'-methoxyphenyl)-5-chloro-
- benzotriazole
- 2-(2'-Hydroxy-4'-ethoxyphenyl)-5-chloro-
- benzotriazole
- 10 2-(2'-Hydroxy-4'-propoxyphenyl)-5-chloro-
- benzotriazole
- 2-(2'-Hydroxy-5'-methylphenyl)-5-chloro-
- benzotriazole
- 2-(2'-Hydroxy-5'-ethylphenyl)-5-chloro-
- 15 benzotriazole
- 2-(2'-Hydroxy-5'-propylphenyl)-5-chloro-
- benzotriazole

The ultraviolet ray absorbents may be used alone or in a mixture of two or more, and they may be

20 added to a dye bath together with the dye composition of the present invention. In this case, the amount thereof is not particularly limited and usually from 0.5 to 5% by weight based on the weight of the materials to be dyed.

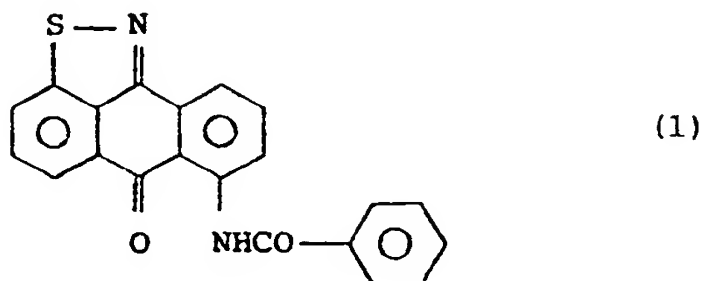
25 In the present invention, the dyeing of polyester fiber materials can be carried out by a conventional exhaustion dyeing, printing or continuous dyeing method. In carrying out the exhaustion dyeing,

1 a dye bath is prepared by dispersing a predetermined
amount of the dye composition of the present invention
in an aqueous medium, if desired together with the
ultraviolet ray absorbent, and then adjusting the pH
5 within a range of 4 to 5 using acetic acid or an aqueous
buffer solution comprising, for example, acetic acid and
sodium acetate. If desired, some quantity of a
sequestering agent, a level dyeing agent of the like
may be added thereto. To the dye bath prepared, fiber
10 materials to be dyed are added, and the bath is heated
gradually (for example, at a rate of 1 to 3°C per minute).
Dyeing can be continued at a predetermined temperature
of higher than 100°C (for example, 110° to 135°C) for
30 to 60 minutes. The dyeing time may be shortened
15 depending on the dyeing state. After the dyeing is
over, the bath is cooled. The dyed materials can be
finished in a conventional manner, for example, washed
with water, if desired subjected to reduction clearing,
followed by washing with water, and then dried. The
20 dye composition of the present invention may be used
alone or in a mixture thereof with other color dyes such
as red dyes and blue dyes. In the above exhaustion
dyeing, the present dye composition can exhibit an
excellent exhaustion dyeing property.

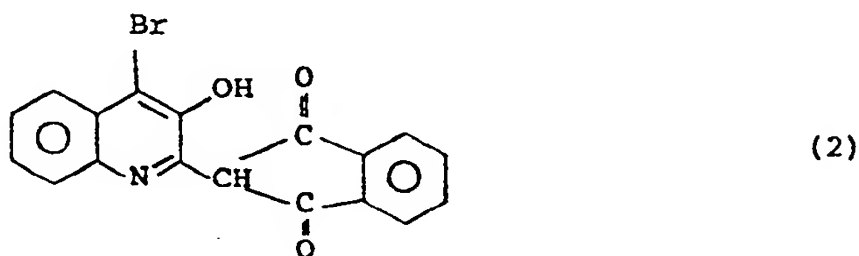
25 The present invention is illustrated in more
detail with reference to the following Examples and
Comparative Examples, wherein parts and % are by weight.

1 Example 1

88 Parts of a yellow disperse dye which has been prepared by finely pulverizing a mixture of 30% of a dye of the following formula (1),



5 and 70% of an anionic surfactant in an aqueous medium, and then drying the resultant, and 12 parts of a yellow disperse dye which has been prepared by finely pulverizing a mixture of 30% of a dye of the following formula (2),



10 and 70% of an anionic surfactant in an aqueous medium, and then drying the resulting aqueous dispersion, were mixed with each other to obtain 100% parts of a yellow disperse dye composition.

1000 Parts of a dye bath of the dye dispersion

1 containing 1.0 part of the yellow disperse dye composi-
tion was prepared and adjusted to pH 5 using acetic
acid and sodium acetate. To the dye bath was added
100 parts of polyester raising textile fabric. The
5 temperature was raised to 60°C, and subsequently raised
upto 130°C at a rate of 1°C per minute. Dyeing was
continued for 60 minutes at 130°C, and then the fabric
was subjected to reduction clearing in a conventional
manner, and dried to obtain a dyed product of a yellow
10 color.

Comparative Example 1

Using 1.0 part of a yellow disperse dye which
has been prepared by finely pulverizing a mixture of
30% of the dye of the aforesaid formula (b) and 30%
15 of an anionic surfactant in an aqueous medium, and
then drying the resulting aqueous dispersion, dyeing
was carried out in the same manner as in Example 1 to
obtain a dyed product of a yellow color.

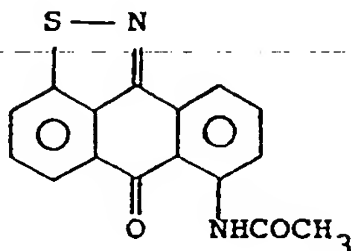
Comparative Examples 2 and 3

20 Using each of the yellow disperse dyes (1) and
(2) in each amount of 1.0 part, dyeing was carried out
in the same manner as in Example 1 to obtain each dyed
product of a yellow color.

Comparative Example 4

25 Using 1.0 part of a yellow disperse dye which

- 1 has been prepared by finely pulverizing a mixture of 30% of a dye represented by the following formula (c),



(c)

dyeing was carried out in the same manner as in Example 1 to obtain a dyed product of a yellow color.

- 5 The exhaustion property of the present dye composition used in Example 1 and the disperse dyes used in Comparative Examples 1, 2, 3 and 4 was observed visually, and the dyed products obtained in Example 1 and Comparative Examples 1, 2, 3, and 4 were measured
10 for their light fastness and sublimation fastness. The results obtained are as shown in Table 1, which demonstrates that the dye composition and the dyed product obtained in Example 1 are superior to those in Comparative Examples 1, 2, 3 and 4 in the exhaustion
15 property, and fastness properties to light and sublimation, respectively.

Table 1

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	Exhaustion property	Light fastness (grade)	Sublimation fastness (grade)
Example 1	○	3-4	3-4
Comparative Example 1	○	3-4	1-2
Comparative Example 2	X	3-4	3-4
Comparative Example 3	○	1-2	3
Comparative Example 4	○	3-4	1-2

1 Test method:

1) Exhaustion property

After the dyeing was over, the exhausted bath was visually observed.

5 ○ : Little residues

X : Many residues

2) Light fastness

The dyed product was backed with urethane foam, exposed to a fade meter (temperature of a black pannel 83°C) for 300 hours, and then judged using a grey scale for assessing change in color.

3) Sublimation fastness

According to JIS L 0879-1968, the dyed product was treated at 185°C for 30 seconds together with undyed polyester cloth for assessing staining.

1 Moreover, using the same yellow disperse dye
composition as in Example 1 and the yellow disperse dyes
which are known to have a practical exhaustion property
and the same as in Comparative Examples 1, 3 and 4, as a
5 yellow component, C.I. Disperse Red 191 (Sumikaron
Brilliant Pink SE-RL, commercially available, manufactured
by Sumitomo Chemical Co.) as a red component, and C.I.
Disperse Blue 54 (Sumikaron Blue S-2GL, commercially
available, manufactured by the same company as above) as
10 a blue component, in a mixing ratio as shown in Table 2,
a blend dyeing was carried out in the same manner as
in Example 1 to obtain each dyed product of a grey color.
The dyed product was subjected to heat-set treatment at
175°C for 5 minutes, and then judged for the change in
15 color using a JIS grey scale for assessing the change.
Table 2 demonstrates that the dye composition in Example
1 is extremely superior in the thermal resistance to
the dyes in Comparative Examples 1, 3 and 4, which are
known to have a practical exhaustion property.

Table 2

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	Blending recipe % o.w.f.			Change in color by heat-set treatment (grade)
	Yellow component	Red component	Blue component	
Example 1	0.15	0.9	0.6	4
Comparative Example 1	0.15	0.9	0.6	2
Comparative Example 3	0.15	0.9	0.6	2-3
Comparative Example 4	0.15	0.9	0.6	2

1 Examples 2 to 7

The dye of the formula (1) and the dye of the formula (2) used in Example 1 were mixed in each mixing weight ratio as shown in Table 3 to obtain each yellow disperse dye composition. Each dye composition exhibited an excellent exhaustion property and gave each dyed product excellent in light fastness and thermal resistance.

Table 3

Example No.	Mixing weight ratio		Exhaustion property	Light fastness (grade)	Sublimation fastness (grade)
	Dye (1)	Dye (2)			
2	80	20	○	3-4	3-4
3	70	30	○	3-4	3-4
4	60	40	○	3-4	3-4
5	40	60	○	3-4	3
6	20	80	○	3	3
7	95	5	○ - Δ	3-4	3-4
Comparative 5	10	90	○	2-3	2-3

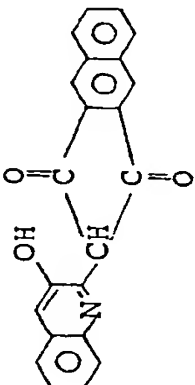
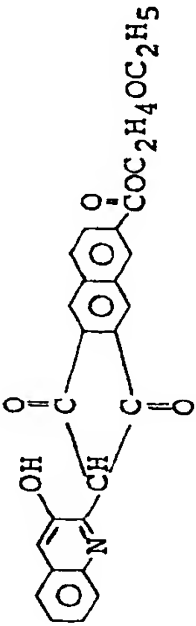
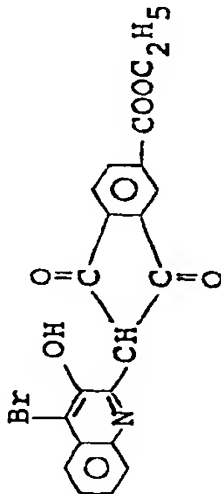
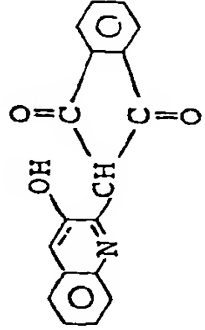
1 Examples 8 to 11

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Example 1 was repeated, provided that each dye as shown in Table 4 was used in place of the dye of the formula (2). Each dye composition obtained exhibited
5 an excellent exhaustion property and gave each dyed product excellent in light fastness and thermal resistance.

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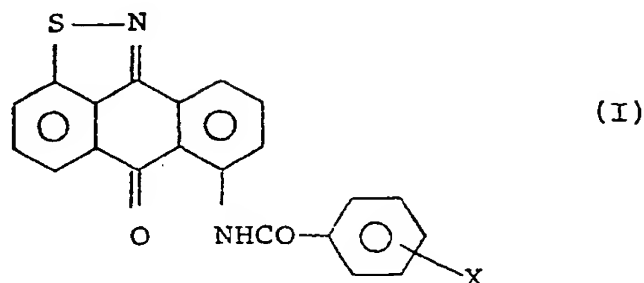
Table 4

Example No.	Dye used in place of the dye (2)	Exhaustion property	Light fastness (grade)	Sublimation fastness (grade)
8		○	3-4	3-4
9		○	3-4	3-4
10		○	3-4	3-4
11		○	3-4	3-4

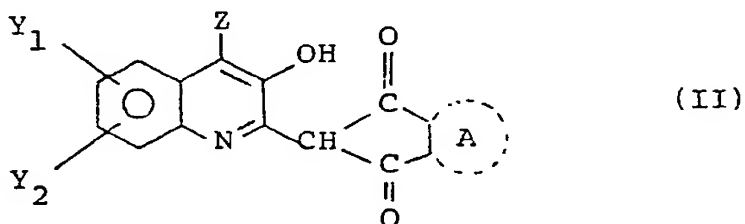
WHAT IS CLAIMED IS:

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1. A water-insoluble disperse dye composition comprising a combination of a dye represented by the following formula (I),



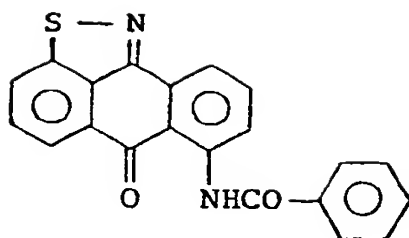
wherein X is hydrogen, halogen, C_1-C_4 alkyl or C_1-C_4 alkoxy, in an amount of 95 to 20% by weight, and a dye represented by the following formula (II),



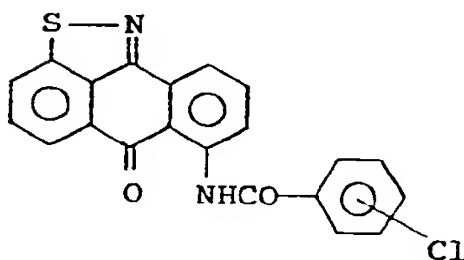
wherein Z, Y_1 and Y_2 are independently hydrogen or halogen, and the ring A is a benzene or naphthalene ring unsubstituted or substituted with a carboxylic acid ester group, in an amount of 5 to 80% by weight.

2. The dye composition according to Claim 1, wherein the dye represented by the formula (I) is a dye of the following formula,

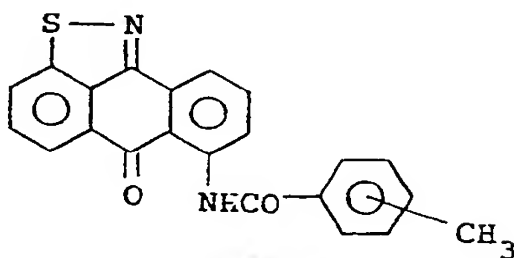
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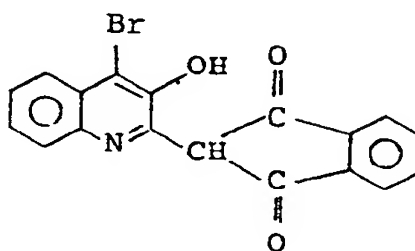
of the following formula,



or of the following formula,

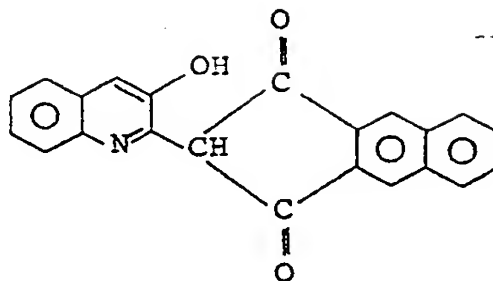


3. The dye composition according to Claim 1,
wherein the dye represented by the formula (II) is a dye
of the following formula,

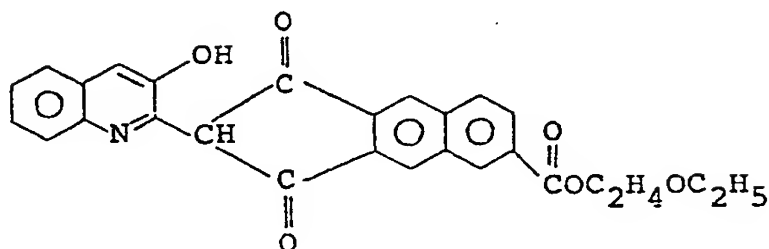


of the following formula,

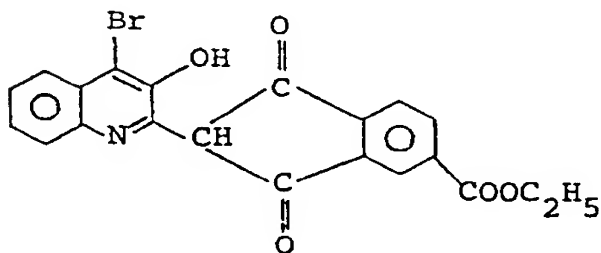
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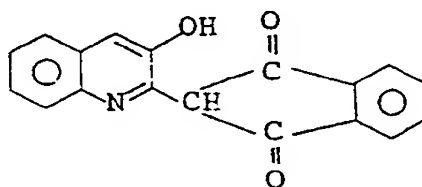
of the following formula,



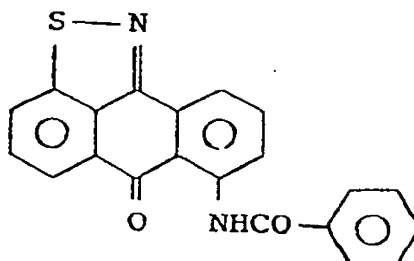
of the following formula,



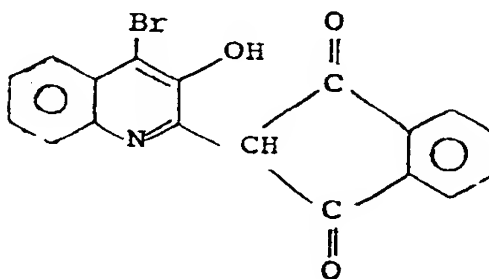
or of the following formula,



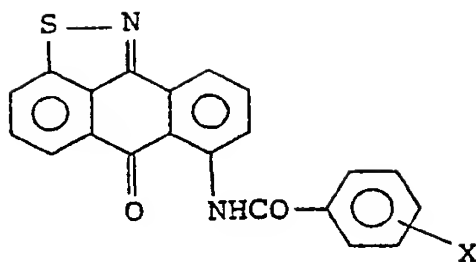
4. The dye composition according to Claim 1, wherein the dye represented by the formula (I) is a dye of the following formula,



and the dye represented by the formula (II) is a dye of the following formula,



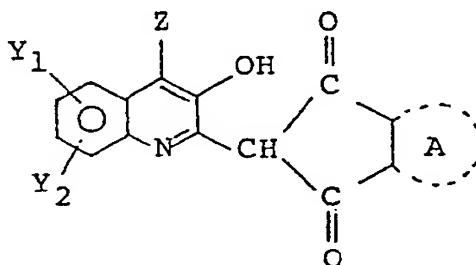
5. A method for dyeing polyester fiber materials, which comprises using a water-insoluble disperse dye composition comprising a combination of a dye represented by the following formula (I),



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(I)

wherein X is hydrogen, halogen, lower alkyl or lower alkoxy, in an amount of 95 to 20% by weight, and a dye represented by the following formula (II),



(II)

wherein Z, Y₁ and Y₂ are independently hydrogen or halogen, and the ring A is a benzene or naphthalene ring unsubstituted or substituted with a carboxylic acid ester group, in an amount of 5 to 80% by weight.

12 EUROPEAN PATENT APPLICATION

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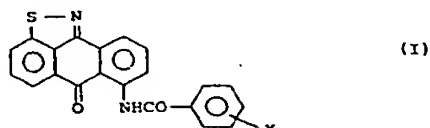
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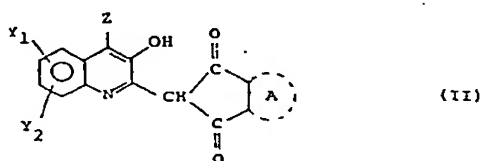
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54 Water-insoluble disperse dye composition.

57 A water-insoluble disperse dye composition comprising
 a combination of a dye represented by the following formula
 (I),



wherein X is hydrogen, halogen, lower alkyl or lower alkoxy,
 in an amount of 95 to 20% by weight, and a dye represented
 by the following formula (II),



wherein Z, Y₁ and Y₂ are independently hydrogen or halogen,
 and the ring A is a benzene or naphthalene ring unsubstituted
 or substituted with a carboxylic acid ester group, in an
 amount of 5 to 80% by weight, which is useful for dyeing
 polyester fiber materials to obtain dyed products having both
 extremely high light fastness and excellent thermal resist-
 ance.



European Patent
Office

EUROPEAN SEARCH REPORT

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Application Number

EP 86 10 8748

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 164 223 (SUMITOMO) * Whole document *	1-5	D 06 P 1/16 D 06 P 3/54 C 09 B 67/22
A	DE-A-1 960 868 (SANDOZ AG) * Page 14, dyes K,L *	1-5	
A	FR-A-2 077 227 (HOECHST) * Page 6, example 2, first formula; page 8, example 4, first formula *	1,3-5	
A	GB-A-1 548 227 (CIBA-GEIGY AG) * Page 6, dye 14; page 9, dye 34 *	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			D 06 P C 09 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16-10-1989	Examiner DELZANT J-F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	